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MASS SPECTROMETRIC INVESTIGATIONS OF ORGANIC PEROXIDES

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The mass spectrometric investigation of cyclic peroxides recently published by Bertrand, Fliszár and Rousseau[1], with the conclusion that "the cyclohexyl ring is less stable than the heterocycle toward electron bombardment" seemed rather astonishing. It was felt that a reinvestigation, using high resolution mass spectrometry and a temperature of the ionizing chamber well below the destruction temperature of the peroxide, might be of interest. Recently Story et al.[2] have also urged such a reinvestigation. When using cyclic dimeric peroxides in a general synthesis of macrocyclic compounds, these workers found different product ratios (GLC) for photolysis and thermolysis.

The results of the high resolution mass spectrometric measurements given below are in excellent accordance with the findings and proposals of Story et al. The spectrum obtained by direct introduction is shown in Fig. 1, and that obtained by indirect introduction (thermolysis at 190°C) in Fig. 2. Mass ratios are given in per cent of the most intense peak, m/e 55 in spectrum 1, and m/e 44 (carbon dioxide)in spectrum 2. The temperature of the ionizing chamber was in both cases 155°C, the ionizing voltage 70 eV, and ionization current 100 μA. The peaks discussed were measured at resolution 15 000 with a double focusing mass spectrometer AEI/GEC MS 902.x)

x) Thanks are due to Cand.mag. Georg Hvistendahl for performing the measurements.

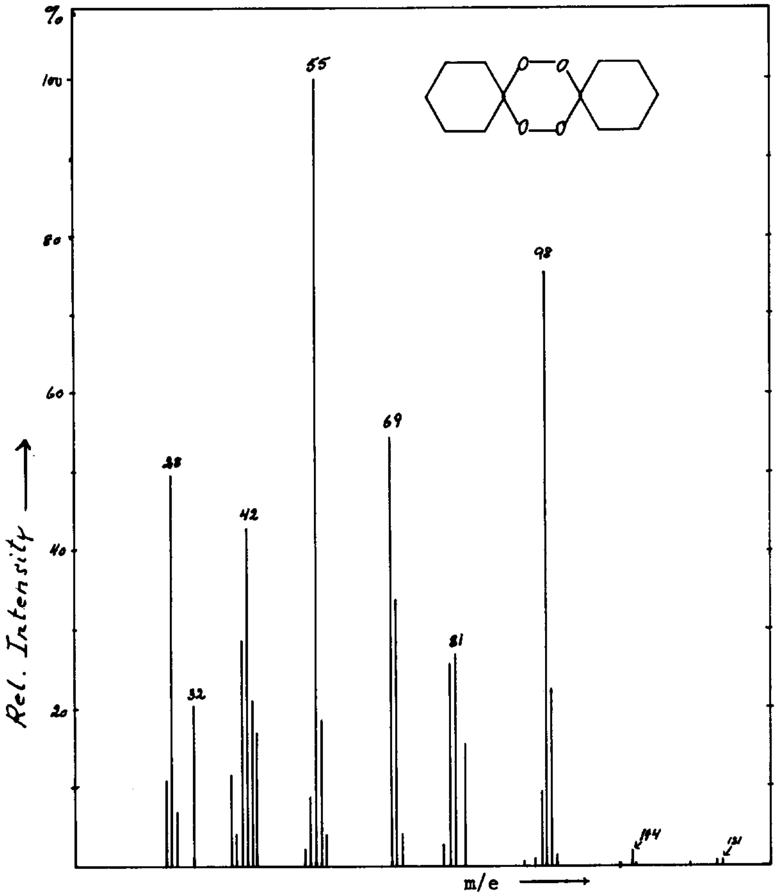
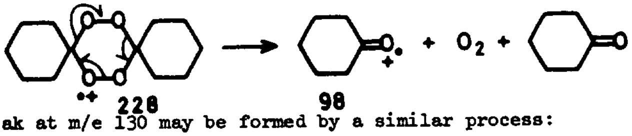
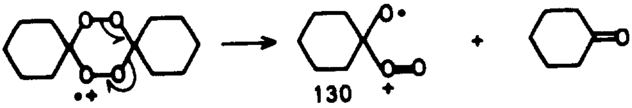


Fig. 1. Spectrum of diperoxide of cyclohexanone, direct introduction.

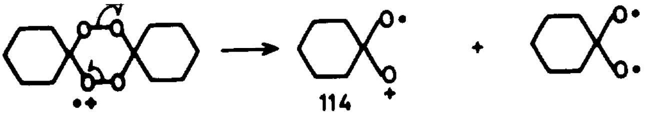
The molecular ion was undetectable in both cases. The two spectra are, however, very different. In spectrum 1 the main reaction may be depicted as follows:



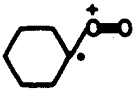
A very small peak at m/e 130 may be formed by a similar process:



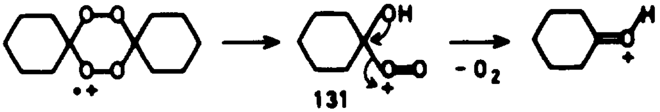
Homolytic cleavage of both the peroxidic bonds may give the m/e 114:



This may lose a hydroxy group resulting in the m/e 97. The m/e 114 may also exist in the forms:



The m/e 131, $C_6H_{11}O_3$, may be formed analogous to m/e 130, but with transfer of a hydrogen radical. Loss of oxygen may then give the m/e 99, $C_6H_{11}O$:



The other characteristic features of spectrum 1 are the rather intense peak m/e 32 (oxygen), and peaks in common with those in a spectrum of cyclohexanone.

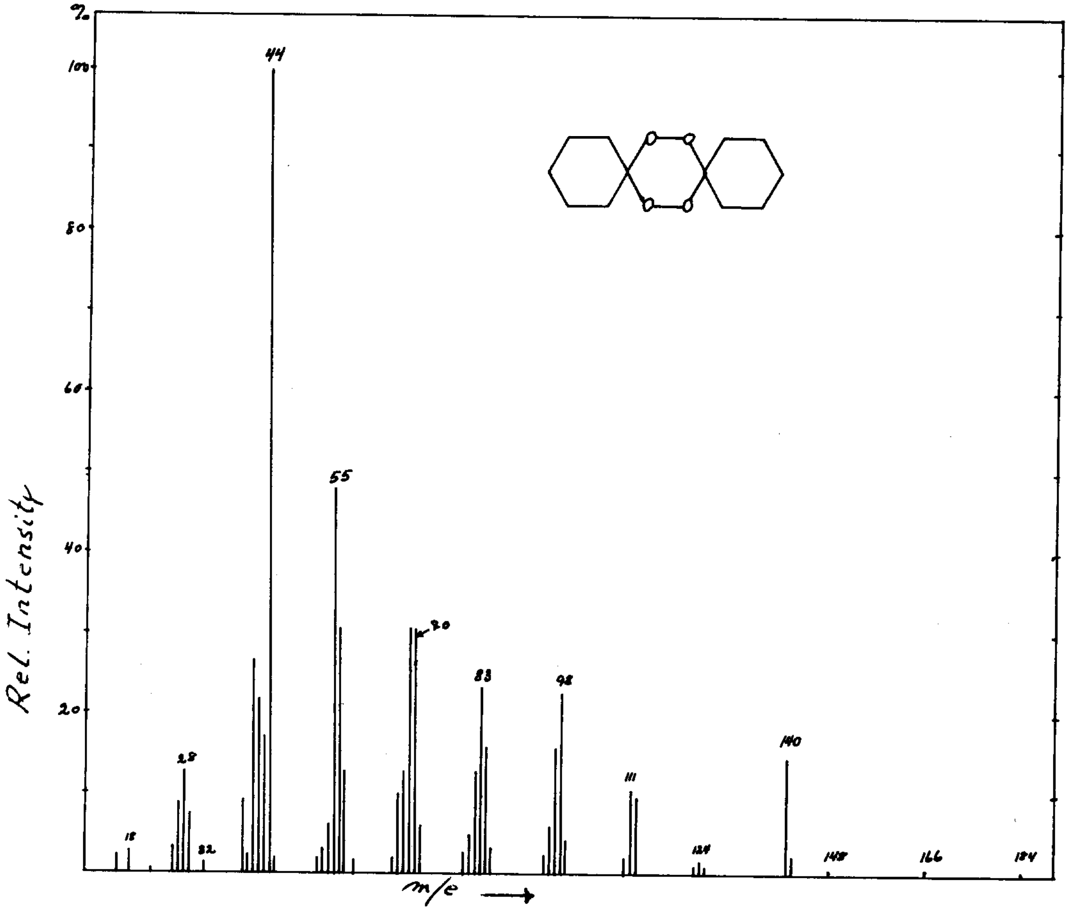
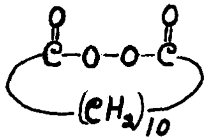


Fig. 2. Spectrum of diperoxide of cyclohexanone, indirect introduction at 190°C.

Spectrum 2, obtained by indirect sample introduction at 190°C, has its most intense peak at m/e 44 (carbon dioxide). The m/e 32 (oxygen) has nearly disappeared in this case. Besides cyclohexanone and its subfragments, fragments of higher m/e, not present in spectrum 1, appear. The most intense of these is m/e 140, $C_{10}H_{20}$, and the highest m/e observed is m/e 184. These two peaks correspond to cyclodecane and 11-undecanolactone, the two thermylysis products isolated by Story et al.[2].

The m/e 112 and m/e 111, C_8H_{16} and C_8H_{15}, may be formed from the cyclodecane molecular ion by loss of ethylene and an ethyl radical respectively.

Differences in relative intensities in spectrum 1 and 2 of the m/e 97-98, 83-84, 69-70 and 55-56 may mainly originate from the cyclodecane and its sub-fragments in spectrum 2. The m/e 166, $C_{11}H_{18}O$, and m/e 148, $C_{11}H_{16}$, may be fragments formed from the 11-undecanolactone by loss of one and two molecules of water. The fact that no molecular ion is observed, does not exclude a transient existence of the primary rearrangement intermediate postulated by Story et al.[2]:



From the present investigation it may safely be concluded that the tetraoxa-cyclohexane ring of the dimeric peroxide is, as one would expect, less stable toward electron impact than the cyclohexylidene ring, a conclusion in conflict with that of Bertrand and al.[1] Both a symmetric and an asymmetric cleavage of the peroxidic ring seems to occur initially, followed by loss of oxygen and formation of the parent ketone of the peroxide, cyclohexanone. Under the conditions of thermolysis a fragmentation pattern very different from that of electron impact, results. However, by thermolysis also, the peroxidic ring seems to be cleaved first, followed by expulsion of carbon dioxide and formation of 11-undecanolactone and cyclodecane. Byproducts other than cyclohexanone may only be formed in minor amounts. The present investigation may also show the importance of: 1) using high resolution to enable a safe identification of the different fragments, 2) using temperatures matched to the sample stability, and 3) measuring with direct as well as with indirect sample introduction in order to differentiate between the effect of electron impact and that of temperature, when dealing with peroxidic compounds.

REFERENCES

1) M. Bertrand, S. Fliszár and Y. Rouseau, J.Org.Chem. 33 (1968) 1931.
2) P.R. Story, D.D. Denson, C.E. Bishop, B.C. Clark, Jr. and J.C. Farine, J. Am. Chem. Soc. 90:3 (1968) 817.